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CHEMISTRY OF POLYNITROETHANE DERIVATIVES

FINAL REPORT

K. Baum, S. S. Bigelow, D. Tzeng and T. G. Archibald

June 1988

U. S. ARMY RESEARCH OFFICE

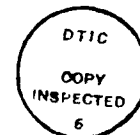
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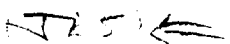
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FIELD 07	GROUP 03	1,1-Diododinitroethylene; 1,1-Diamino-2,2-dinitroethylenes; 2,2-Dinitro-3,3-trifluoroethanol; Bis(2,2-dinitro-3,3,3-trifluoroethyl) formal	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The nitration of tetraiodoethylene was shown to give 1,1-diiododinitroethylene, and reactions of this olefin with nucleophiles were studied. Phenol and trifluoroethanol in the presence of base gave the corresponding α,α-dinitroorthoacetates. Primary and secondary amines reacted with 1,1-diiododinitroethylene to give the corresponding 1,1-diamino-2,2-dinitroethylene derivatives. The reaction of ammonia with 1,1-diiododinitroethylene gave ammonium cyanodinitromethide. Fluoride ion and 1,1-diiododinitroethylene gave 1,1-dinitro-2,2,2-trifluoroethane, which was reacted with aqueous formaldehyde to give 2,2-dinitro-3,3,3-trifluoropropanol. Reaction of 2,2-dinitro-3,3,3-trifluoropropanol with trioxane and sulfuric acid gave bis(2,2-dinitro-3,3,3-trifluoropropyl)formal.</p>			
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Introduction

This final report summarizes work on Contract DAAG29-85-C-0010, during the period 1 May 1985 through 30 April 1988. This work is a continuation of research supported by the Army Research Office under Contracts DAAG29-82-C-0003 and DAAG29-79-C-0011.

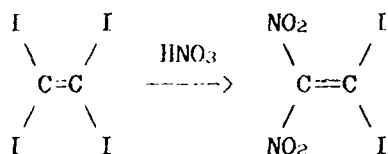
Polynitroolefins are of general theoretical interest for studies of the bonding effects of electronegative organic substituents. They are also of practical interest as building blocks for energetic explosives and propellant ingredients. Under the predecessor ARO contracts, evidence for the formation of tetranitroethylene in solution thermolysis was obtained by Diels Alder trapping experiments,¹ and subsequently the pure olefin was isolated by flash vacuum pyrolysis.² The generality of this novel N_2O_4 extrusion was demonstrated with several additional examples. Pyrolysis of the anthracene adduct of tetranitroethylene gave 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene,³ the Diels Alder adduct of the unknown dinitro-acetylene. The pyrolysis of 1,2-difluorotetranitroethane gave 1,2-difluorodinitroethylene, the characterization of which was pursued under the current contract. 

Under this program, basic research on the chemistry of nitro compounds was continued. Emphasis was placed on exploration of routes to dinitroacetylene, which is a potential precursor to polynitro cage compounds.

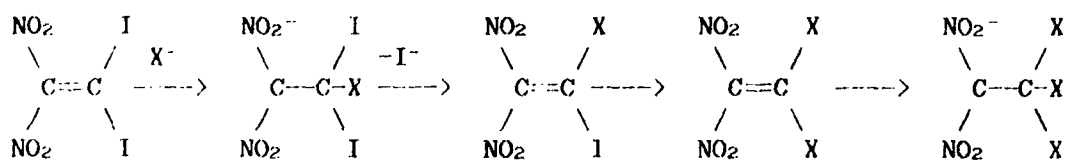
Discussion

One possible route to dinitroacetylene is reductive elimination of 1,2-diiododinitroethylene. This compound was reported in 1900 by the nitration of tetraiodoethylene.⁴ We repeated the work and found that the

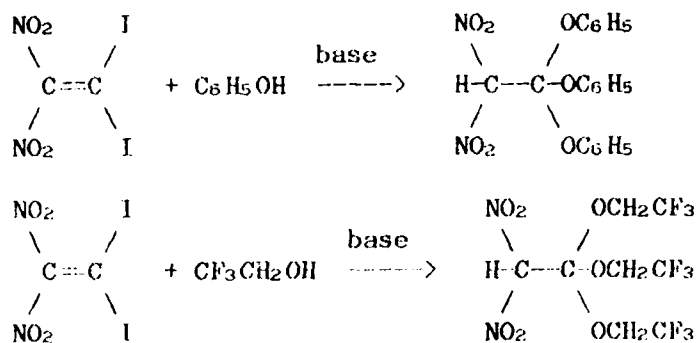
^{13}C NMR spectrum of the nitration product was consistent with the isomer of the reported structure, 1,1-diiododinitroethylene. The ^{13}C spectrum showed singlets at δ 29 and 157, whereas the reported structure would show a single peak. The δ 29 signal is in the region reported for other *gem*-diiodo olefins and the δ 157 chemical shift is compatible with the *gem*-dinitro carbon. The assigned structure was confirmed by x-ray crystallography. An interesting feature of the structure is that only one nitro group is coplanar with the double bond and the other is twisted out of plane by 90° .



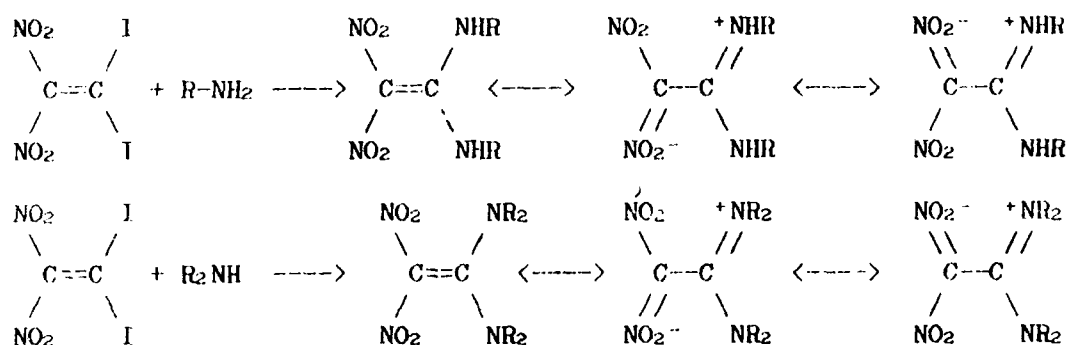
Although this structure is unlikely to lead to dinitroacetylene, it appeared to be useful for reactions with nucleophiles; alternate Michael additions and iodide eliminations could give new disubstituted dinitroolefins, as well as trisubstituted nitronate salts.



Consequently, reactions of some nucleophilic reagents with 1,2-diiodo dinitroethylene were screened. Thus, phenol in aqueous sodium hydroxide and trifluoroethanol in the presence of potassium carbonate gave the corresponding orthoesters after acidification.



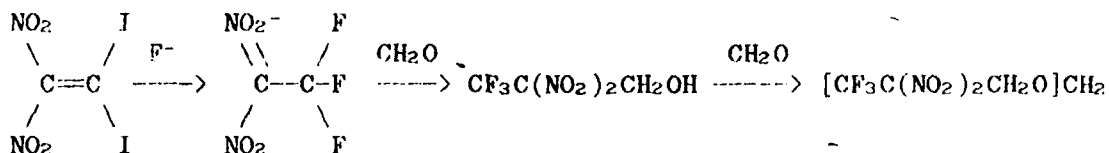
Primary and secondary amines reacted with 1,1-diiododinitroethylene to give the corresponding diaminodinitro "olefins". Spectral properties and x-ray analysis showed that the products possess zwitterionic character.



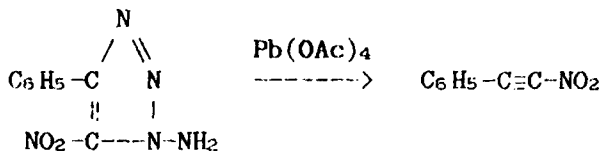
The reaction of ammonia with 1,1-diiododinitroethylene was of particular interest because the product analogous to those above would be a potential explosive balanced for autocombustion to CO. The product obtained, however, was identified as ammonium cyanodinitromethide, $\text{NH}_4^+\text{NC-C}(\text{NO}_2)_2^-$. Cyanodinitromethide salts have been prepared previously by other methods.⁵

Fluoride ion reacted with 1,1-diiododinitroethylene to give the trifluoromethyl nitronate salt. Formylation with aqueous formaldehyde gave 2,2-dinitro-3,3,3-trifluoropropanol, a new and potentially versatile building block for propellant and explosives applications. Reaction of 2,2-dinitro-

3,3,3-trifluoropropanol with trioxane and sulfuric acid gave bis(2,2-dinitro-3,3,3-trifluoropropyl)formal, the fluorinated analog of BDNPF, a widely used energetic plasticizer.



The oxidation of aminotriazoles with lead tetraacetate has been reported to generate benzynes.⁶ The feasibility of using this reaction for the synthesis of nitroacetylenes was investigated using 1-amino-5-nitro-4-phenyl-1,2,3-triazole. The lead tetraacetate reaction gave nitrophenylacetylene, based on comparison of its IR spectrum with that reported.⁷ This approach was not pursued because of difficulties in preparing starting materials, and because project resources were needed for the diiododinitroethylene work.



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